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EFFECT OF CARBON ON ION BEAM MIXING OF Fe-Ti BILAYERS

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ABSTRACT

The influence of implanted carbon on ion beam mixing of a Fe-Ti system was investigated. Carbon was introduced into bilayer samples by implanting ^{13}C isotopes. The implantation energies were selected to set the mean range of carbon ions in either the iron or titanium layer. The effect of implanted carbon on 400 keV Ar ion mixing in the temperature range from 0 to 300 °C was studied using Rutherford backscattering spectroscopy at the energy of 5 MeV. Changes in carbon concentration profiles were probed utilizing the resonance of the nuclear reaction $^{13}\text{C}(p,\gamma)^{14}\text{N}$ at the proton energy of 1.748 MeV. The measurements revealed that mixing was not affected by carbon implanted into the titanium layer. However, carbon in the iron layer remarkably retarded mixing at all temperatures investigated. Significant changes in carbon depth distributions were observed only when the sample with implanted carbon in the iron layer was mixed at 300 °C. These results are explained in terms of the enhanced mobility of carbon in an evaporated iron film which allows segregation to the interface. At low temperatures, however, vacancy-carbon interaction in iron may have a contribution to the retarded ion beam mixing.

INTRODUCTION

The tribological performance of Fe-Ti-C surface films produced by energetic beams has been firmly established in recent years [1,2]. Ion implantation, ion beam mixing, and excimer laser mixing have been successfully used in the manufacturing of these films [1-3]. Extensive microstructure studies have revealed either an amorphous microstructure, an amorphous microstructure with finely dispersed titanium carbide precipitates, or embedded iron carbides in ferritic iron matrix as a result of these energetic processes. Tribological properties have been correlated with the observed microstructures [1,2,4].

Studies involving Fe-C, Ti-C, and Fe-Ti-C layered systems have shown that the production of well mixed Fe-Ti-C films by ion beam mixing is difficult to achieve [5]. Of these systems Fe-C has a positive whereas Ti-C has a negative heat of mixing. Ion mixing of Fe-C and Ti-C bilayers has shown mixing to be diffusion controlled at elevated temperatures and thermodynamically controlled at low temperatures [5]. Transition into the temperature dependent, radiation enhanced diffusion controlled regime occurs at a lower temperature in the iron-carbon than in the titanium-carbon case. Significant mixing was obtained only in this high temperature regime. In addition, carbide formation was found and believed to play an important role in the mixing dynamics [6]. In fact, titanium carbide has been shown to form a mixing barrier even in the Ni-Si case, which is generally easy to mix [7].

The role of different kinds of point defects in ion beam mixing is not yet completely understood. Some work suggests that the contribution of vacancies in a thermal spike is not as great as that of interstitials [8]. Because of the high concentration of point defects in the collision cascade the addition of elements which interact strongly with the defects will presumably affect the mixing behavior. This has been observed in ion beam mixing of hydrogenated titanium with iron and nickel [9]. In the nickel case the mixing rate was almost unaffected while the mixing rate of iron was greatly retarded.

In the present work we have continued to examine the effects of additional elements on ion mixing by studying the role of carbon on ion beam mixing of Fe-Ti bilayer samples. In particular we have addressed the question of what role placing carbon in iron or titanium plays on the mixing of the Fe/Ti system.

EXPERIMENTAL METHODS AND MEASUREMENTS

Iron and titanium layers were evaporated by using an e-gun in a vacuum chamber with a base vacuum 1×10^{-8} torr. Vacuum during evaporation was typically in the area of 10^{-7} torr. The thicknesses of iron and titanium layers were 80 and 120 nm, respectively. Silicon wafers with a thick layer of SiO_2 were used as substrates. The titanium layer was deposited first and iron was the topmost layer.

Part of the samples were implanted with ^{13}C at the energies of 32 and 100 keV. These energies were chosen to produce corresponding ranges that were either in the iron or titanium layer. The implanted fluence was 5×10^{16} ions/cm². During implantation the samples were cooled to temperatures below 0 °C. Implantation was carried out in a vacuum of 10^{-6} torr, and a liquid nitrogen cold trap was used to reduce contamination.

Ion beam mixing was carried out with 400 keV Ar ions at a dose of 2×10^{16} ions/cm². The calculated range was adequate [10] insuring that most of Ar ions penetrated the Fe-Ti interface. The mixing temperature was varied with studies carried out at 0, 150, and 300 °C.

The amount of mixing was probed by using He^{++} Rutherford backscattering spectroscopy (RBS) at 5 MeV. At this energy the scattering of He^{++} by iron and titanium is still Rutherford, but the mass resolution is remarkably improved as compared to measurements at lower energies. Carbon concentrations were measured utilizing the resonance of the $^{13}\text{C}(p,\gamma)^{14}\text{N}$ at the proton energy of 1747.6 keV [11]. Because the width of this resonance is 70 eV, the depth resolution was determined by the energy resolution 1.6 keV of the accelerator. The depth resolution at the surface was 20 nm.

RESULTS AND DISCUSSION

In Fig. 1 RBS spectra taken from samples mixed at 0 and 300 °C with and without carbon implantation are shown. Mixing is clearly obvious in the unimplanted sample as well as in the sample with implanted carbon in the titanium layer. However, mixing in the sample which had C implanted into the iron layer is significantly retarded. This effect is most striking in the 300 °C data. It is interesting to note that despite of the retarded mixing in the sample with carbon in the titanium layer, the titanium and iron distributions exhibit an interdiffusion like profile. However, in the carbon in iron case at 300 °C the iron profile at the Fe/Ti interface is relatively sharp but has a low concentration tail into titanium which suggests a "leak flux" type of diffusion through the interface.

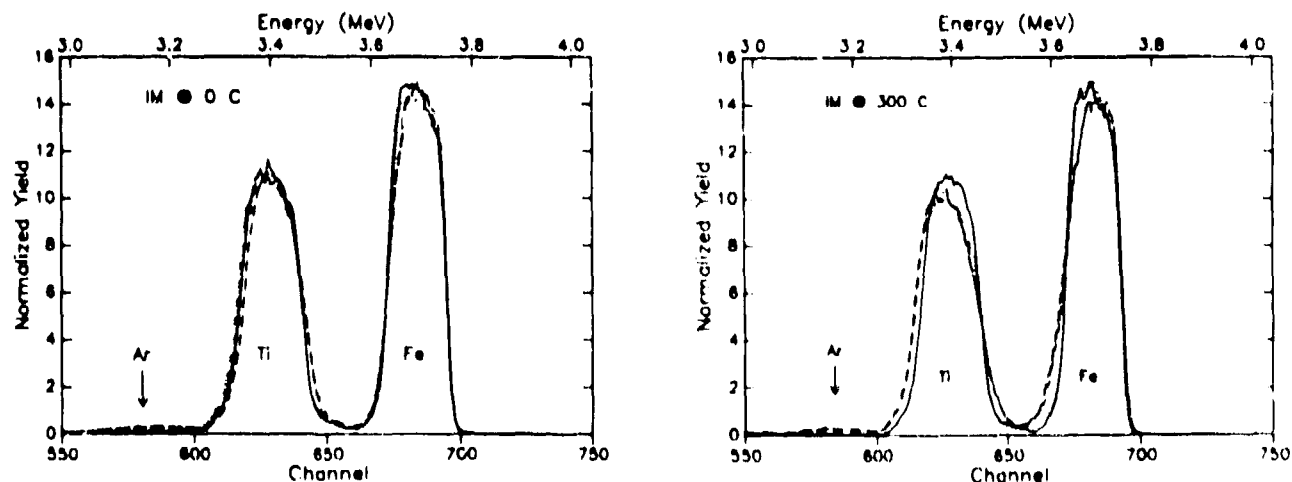
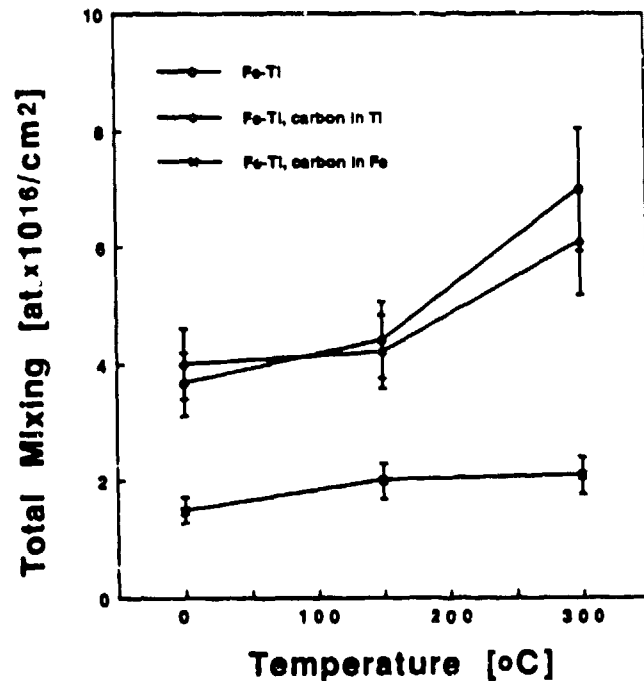


Fig. 1. RBS spectra of the Fe-Ti as-deposited sample (—), and the ion beam mixed samples Fe-Ti (---), Fe-Ti with carbon in titanium (---), and Fe-Ti with carbon in iron (---) at 0 and 300 °C.

Mixing in different samples is further illustrated in Fig. 2, where the amount of mixing vs. mixing temperature is shown. The amount of mixing in Fig. 2 is the total amount of Fe and Ti in the mixed zone. As can be seen in this figure the mixing rate of the unimplanted sample and the sample with implanted carbon in the titanium layer are about the same. It is interesting to note that mixing in the sample with carbon in the iron layer is almost independent of temperature in addition to a lower mixing rate.

Carbon distributions are shown in Fig. 3. These data show that the initial carbon distribution in iron is bimodal deviating from the expected implant distribution which is observed in the titanium case. The calculated range for 32 keV carbon in iron is 42 nm [10] giving evidence that diffusion of carbon in iron has occurred during or after the implantation process. This

Fig. 2. Total mixing of the Fe-Ti, Fe-Ti (carbon in titanium), and Fe-Ti (carbon in iron) samples as a function of the temperature.



diffusion has resulted in carbon segregation to both the surface and Fe/Ti interface. This phenomena appears to be a property of evaporated iron since similar effects have not been observed for carbon implanted into a well annealed polycrystalline iron plate at the same energy [12]. This observation may be the result of the large grain boundary fraction present in the evaporated film and short-circuit diffusion processes. The enhanced diffusion of impurities such as carbon in evaporated thin films may have a pronounced effect on experimental results of ion beam mixing, because thin films have almost always been utilized in mixing studies.

The carbon distribution in the iron layer after ion beam mixing at 0 °C differs very little from the as-implanted distribution. The total concentration has slightly decreased after mixing at 150 °C, although the shape of the distribution is still bimodal. However, a remarkable change can be observed after mixing at 300 °C. The total amount of carbon has been significantly decreased in the surface region leaving a high carbon concentration at the Fe-Ti interface. The concentration at the interface is the same as after ion beam mixing at 150 °C. Also shown in Fig. 3 is data for the control sample which received the same heat treatment as the sample mixed at 300 °C but without irradiation. These data show no loss of carbon and some segregation to the surface. Contrary to the behavior of carbon in the iron layer the distributions in the titanium layer are almost unchanged.

These results confirm the previous reported data about the retardation of ion beam mixing in the Fe-Ti system by the presence of carbon [13]. However, here we have demonstrated that the effect of carbon in the titanium layer is minimal, whereas carbon in iron strongly suppresses ion beam mixing at concentrations used here

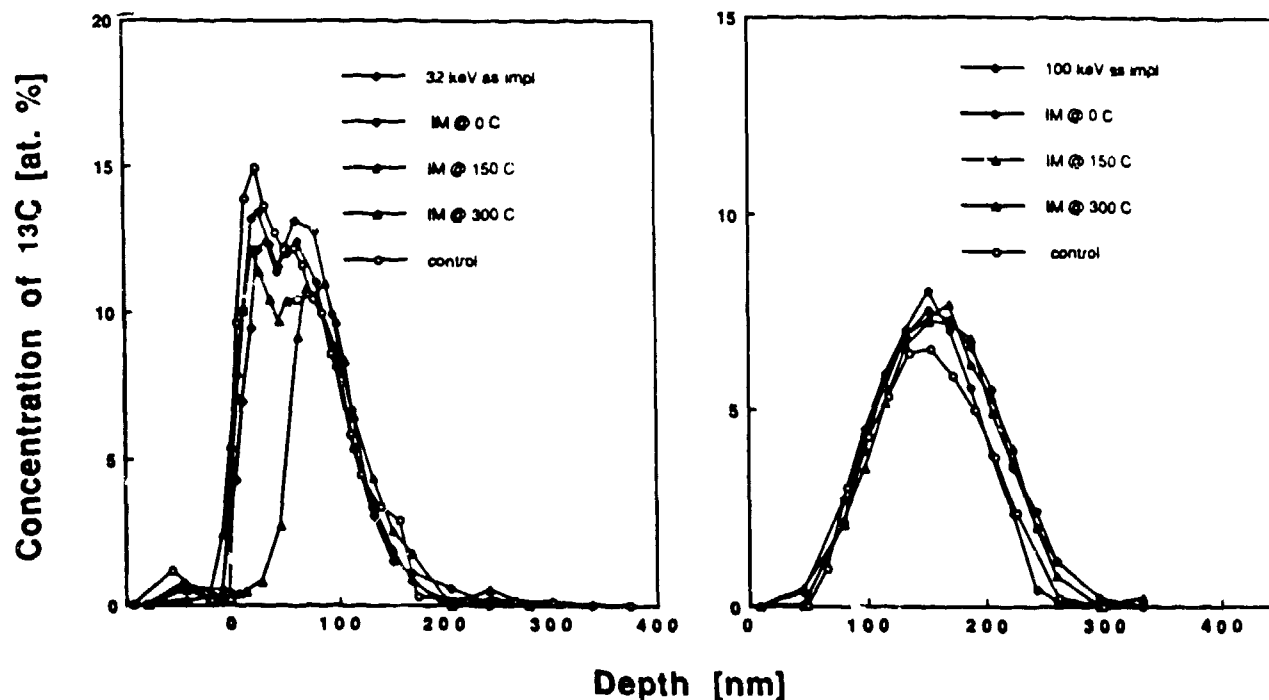


Fig. 3. Carbon distributions in the iron (implantation energy 32 keV) and titanium (implantation energy 100 keV) layers.

The iron distribution after ion beam mixing at 300 °C is unusual. At the interface there is a low concentration tail in the iron distribution which penetrates as deep into the titanium layer as iron in the unimplanted sample and in the sample with implanted carbon in the titanium layer. In fact, the iron distributions at the interface in the samples mixed at different temperatures have almost identical shapes except for the presence this tail. Moreover, this tail does not result from the intermixing of iron and titanium, because there is not corresponding titanium tail penetrating to equal depths in the iron layer. Instead, the iron layer is slightly thinner after ion beam mixing with the loss of material corresponding to the amount in the tail part of the distribution profile. These data indicate that the migration of iron occurred without a corresponding interdiffusion of titanium.

The reason for the differences in the iron distribution profiles in the carbon implanted iron layer, at low and high temperature is obviously the result of the change in the nature of carbon during higher temperature ion mixing. Figure 3 clearly shows that a dramatic change in distribution has occurred during this process. Microstructural data were not available at the time of this writing but studies are in progress.

While the full kinetic and thermodynamic implications resulting from the presence and state of carbon on the mixing of iron and titanium are not well understood it is clear that intermixing has been suppressed. The carbon distribution resulting during ion mixing appears to be responsible for the differences observed in mixing behavior between the two implantation cases. Greater mixing was observed in the carbon in titanium case along with a lower carbon concentration at the interface relative to the carbon in iron case. These data show that interdiffusion and mixing are a function of carbon content. Further evidence for this hypothesis is provided by thermal diffusion studies on $\text{Ti-Fe}_{100-x}\text{C}_x$ diffusion couples, where a closed TiC_{1-x} carbide layer was formed with x -values greater than 0.5, preventing Fe-Ti interdiffusion [14].

It is possible but not evident that the retardation mechanism at 0 and 150 °C is different from that at 300 °C. This is suggested by the different shape of the iron distribution at the interface. One possible retardation mechanism at lower temperatures would be the interaction of carbon with vacancies during ion beam mixing. This situation is analogical to that observed in the ion beam mixing studies of iron and nickel with hydrogenated titanium [9]. In that work a model was proposed which correlated mixing with the trapping energy of hydrogen. This model was further

speculated on by Børgesen et al. [15] who proposed that hydrogen-defect interaction takes place during the early stages of the "cool-down" after a spike.

Vacancies in iron interact also strongly with carbon. In fact, positron annihilation studies [16] show that vacancy-carbon pairs are stable up to 350 K and electron microscope studies [17] suggest a dissociation of vacancy-carbon pairs in iron at 520 K. These temperatures are of course very low as compared to the circumstances in the radiation cascade as pointed out in ref.15. Thus the immobilization of vacancies by impurity trapping during ion beam mixing is unlikely. We propose, a priori, that elements like carbon and hydrogen may have effect on the point defect concentrations during the thermal spike catalyzing for example recombination reactions. This would also be consistent with the microstructure studies on carbon implanted iron, which show no amorphization at concentrations up to 50 at. % [18]. An amorphous phase in this system, however, exists and can be produced by excimer laser melting [19].

CONCLUSIONS

Our studies on the effect of carbon on the ion beam mixing of iron-titanium multilayers reveal a greatly retarded mixing rate if carbon was initially located in the iron layer. No difference was found in mixing rates between carbon free sample and the sample with carbon in the titanium layer. This retardation can be attributed to the enhanced mobility of carbon in evaporated iron films which allows segregation to the Fe-Ti interface. At low temperatures carbon may affect mixing through a mechanism based on the effect of carbon on the mobility or concentration of point defects in iron.

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